



Steam reforming of bio-oil from rice husks fast pyrolysis for hydrogen production

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ARTICLE INFO

Article history:

Received 5 May 2011

Received in revised form 9 July 2011

Accepted 12 July 2011

Available online 21 July 2011

Keywords:

Bio-oil

Steam reforming

Hydrogen production

Ni-based catalyst

ABSTRACT

Steam reforming of two kinds of bio-oil from rice husks fast pyrolysis was conducted for hydrogen production at three temperatures (650, 750 and 850 °C) with Ni-based catalyst in a fixed-bed reactor. The gas composition and organic compounds in liquid condensate were detected by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS), respectively. In addition, the carbon deposition was also investigated. The results showed that the mole fraction range of hydrogen was within 55.8–61.3% at all temperatures and more hydrogen was produced at the higher temperature. The highest H₂ efficiency of bio-oil steam reforming was 45.33% when extra water was added. The bio-oil with lower content of chemical compounds has a higher H₂ efficiency, but its hydrogen volume was less. Analysis of the liquid condensate showed that most of the organic compounds were circularity compounds. The carbon deposition can decrease the bio-oil conversion, and it was easier to form at the temperature of 750 °C.

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1. Introduction

In recent years, energy shortage and environmental problems have become big threats to the sustainable development of our society. With the depletion of fossil energy reserves in the world, renewable energy sources have attracted significant attention. Hydrogen is not only an ideal energy carrier for the future, but also a fundamental raw material and feedstock in petroleum, chemical engineering, chemical fertilizer and metallurgical industries. Traditionally, hydrogen is primarily produced by catalytic steam reforming of natural gas, light hydrocarbons or naphtha (Yan et al., 2010a,b). However, researchers have been paying greater attention to hydrogen production from biomass in recent years. As a renewable energy source, biomass has qualities of clean energy, is cost-effective, CO₂ neutral and has low sulfur content. Two main technologies for hydrogen production from biomass that have been explored are steam gasification of biomass and catalytic steam reforming of bio-oil (Garcia et al., 2000). The latter route begins with fast pyrolysis of biomass to produce bio-oil, followed by catalytic steam reforming.

There is extensive literature on pyrolysis of biomass (Chen et al., 2010; Oasmaa and Czernik, 1999; Oasmaa et al., 1997, 2005; Shen et al., 2010; Tsai et al., 2007; Kim et al., 2010; Seon et al., 2010; Hyeon et al., 2010; Liu et al., 2010; Bridgwater, 1999; Putun et al., 2008; Charles et al., 2008; Lievens et al., 2009; Smith et al., 2009). In the above studies, bio-oils were obtained by decomposing

biomass samples at different pyrolysis conditions. And characteristics of the obtained bio-oil were also investigated by various instrumental techniques. Biomass pyrolysis for bio-oil production is an important technological route. Bio-oil has a much higher energy density than biomass. Bio-oil can be collected from scattered biomass pyrolysis stations easily, and in this process, the transportation costs can be reduced effectively. At present, many research institutes in the world have set up different systems to produce bio-oil. However, until now, the properties of bio-oil are still not very good. High water content, low heating value, high viscosity and corrosiveness (compare with fossil fuel) have limited the extensive use of bio-oil as a liquid fuel. At present, bio-oil is very difficult to use in the engine directly without modification and can be only used as a boiler fuel. Therefore, upgrading of bio-oil is needed to improve its properties for liquid fuel. Different ways, such as bio-oil/diesel emulsion (Chiaramonti et al., 2003), hydro-treatment (Fisk et al., 2009) and steam reforming of bio-oil for hydrogen production (Wu et al., 2008a,b; Wu and Liu, 2010a,b, 2011; Takanabe et al., 2004; Yamazaki and Matsuki, 2006; Rioche et al., 2005) have been investigated. Steam reforming of bio-oil for hydrogen production is one alternative solution for bio-oil utilization. Chornet and co-workers (Marquevich et al., 1999; Wang et al., 1998; Garcia et al., 2000) are the first to have investigated the process of steam reforming of the aqueous fraction of bio-oil, and they have also proposed an integrated process concept of hydrogen production via bio-oil aqueous fraction. They have mainly tested commercial or Ni-based catalysts. In addition, numerous studies on steam reforming of a model compound (acetic acid, m-cresol, phenol, acetone and ethanol) of bio-oil have been reported using steam reforming for hydrogen production (Wu et al., 2008a,b;

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Wu and Liu, 2010a,b, 2011; Takanahe et al., 2004, 2006a,b; Yamazaki and Matsuki, 2006; Rioche et al., 2005). They reported that the bio-oil steam reforming for hydrogen production would seem to be a promising route. However, research conducted on steam reforming of actual bio-oil instead of a model compound of bio-oil is limited (Yan et al., 2010a,b; Xu et al., 2010).

In our previous research (Wu and Liu, 2010a,b, 2011), the model compound of *m*-cresol from heavy bio-oil was chosen as a material for hydrogen production. The carbon deposition and the liquid condensate recycling were also investigated. In addition, we (Chen et al., 2011) investigated the effect of hot vapor filtration (HVF) on improving the quality of bio-oil. Moreover, the effect of selective condensation on the characterization of bio-oil from pine sawdust from fast pyrolysis using a fluidized-bed reactor was investigated (Chen et al., 2010). The condenser and electrostatic precipitator (EP) were used to collect the bio-oil. The water content of bio-oil C₁ (the bio-oil condensed without HVF) and F₁ (the bio-oil condensed with HVF) were 64.41% and 75.09% by weight, respectively. The water content of the bio-oil from the EP was 10.77% and 9.19% by weight without and with HVF, respectively. By weight, 88.9% of water from steam was condensed in the condenser. Because bio-oil condensed in the condenser has such high water content, it cannot be used directly as fuel or for chemical compounds. However, it can be used for hydrogen production through steam reforming.

The main objective of this research was to investigate steam reforming of bio-oil derived from fast pyrolysis of rice husks for hydrogen production with a commercial Ni-based catalyst in a fixed bed reactor. In addition, the properties of gases, liquid condensate and carbon deposition were also investigated.

2. Methods

2.1. Feedstock analyses

The bio-oils C₁ and F₁ were used for steam reforming. The properties of the two bio-oils were shown in a separated paper (Chen et al., 2011). Because chemical composition of the bio-oil is made up of C, H, and O compounds, from the elemental analysis and the water content of the bio-oil, the molecular formula can be calculated. Hydrogen/carbon (H/C) and the oxygen/carbon (O/C) ratios of C₁ are 2.54 and 3.24, respectively, and those of F₁ are 0.64 and 0.78, respectively. Thus the molecular formula of C₁, F₁ bio-oils was CH_{2.54}O_{0.64}, and CH_{3.24}O_{0.78}, respectively.

2.2. Experimental apparatus and procedure

In steam reforming of bio-fuels for hydrogen production, the experiment was carried out based on a fixed-bed reactor system (Fig. 1). The experimental facility includes feeder, reactor, condenser, dryer, gas flow meter, gas collector and gas analyzer. The feeding rate of bio-oil was controlled by a syringe pumps. A catalyst support is fixed in the middle section part of the reactor to support the catalyst. The fixed-bed reactor (height, 800 mm and inner diameter, 15 mm) is fixed in an electric tubular furnace. A thermocouple and automatic temperature controller keep the catalyst bed at a constant reaction temperature. Reaction products are condensed through a condenser. Liquid product and surplus water are collected in a liquid receiver. After drying, the gas product volume is measured by a wet gas flow meter and then collected in a gas bag. The gas product composition was determined by a GC. The wet gas flow meter in this system is used to calculate the gas product yield over the reaction time.

2.3. Analytical methods

The gas composition of the steam reforming of bio-oil was measured by a GC. The water content, chemical composition of the liquid condensate and its carbon deposition were determined.

2.3.1. Gas analysis

Gas analysis was carried out using a gas chromatograph (GC-14B, Shimadzu) equipped with thermal conductivity detector (TCD). Standard gas mixtures were used for calibration, and argon was used as the carrier gas.

2.3.2. Water content

Water content of liquid condensate was analyzed according to ASTM E 203 by Karl-Fischer titration (precision of 0.01% using KFT 870, Swiss Manthon Instrument).

2.3.3. Composition of liquid condensate

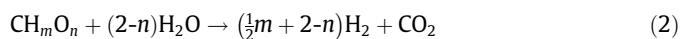
A GC–MS analysis was carried out to identify the chemical compounds of liquid condensate. Pretreatment of liquid samples in the GC/MS method was followed chloroform, which has a volume ratio of 10:1 compared with the liquid condensate samples, was used to extract the chemical compounds. Water in the liquid condensate was absorbed by anhydrous sodium sulfate. The GC–MS system consists of a gas chromatograph coupled to a quadrupole mass spectrometer (GC–MS QP 2010, Shimadzu) using a capillary column (30 m × 0.25 mm i.d.; film thickness, 0.25 μm). Electron ionization (EI) was used with an ion source temperature of 230 °C and interface temperature of 280 °C, maintaining EI spectra at 70 eV. In EI, the instrument was used in SCAN mode initially to confirm the identity of the compounds and then in SIM (selected ion monitoring) mode for quantitative analysis. The GC system was equipped with a split/splitless inlet. The injector temperature was 250 °C. A LEAP Technologies auto sampler with a 10 μL syringe was used for injections of 1 μL at a rate of 10 μL s^{−1}. The carrier gas was helium (UHP) at a constant flow of 1.0 mL min^{−1}. The oven temperature program had an initial temperature of 60 °C held for 2.0 min, rising by 8 °C/min to 300 °C, which was held for 10.0 min with a total run time of 35.0 min. This temperature program was selected to provide adequate separation of most of the compounds of interest.

2.4. Data analysis

In the steam-reforming of bio-oil, products are collected in three phases, gas products (desirable products), solid carbon (carbon deposition), and liquid condensate, respectively. For gas products, the hydrogen efficiency can be calculated according to Eq. (1)

$$\text{H}_2 \text{ efficiency (\%)} = \frac{\text{H}_2(\text{obtained})}{\text{H}_2 \text{ (calculated in stoichiometric potential)}} \quad (1)$$

Hydrogen in stoichiometric potential is based on the ideal reaction shown as Eq. (2)



3. Results and discussion

3.1. Steam reforming of bio-oil for hydrogen production

The bio-oil C₁ and F₁ were used as the feedstock for hydrogen production. In the experiment, three temperatures (650, 750 and 850 °C) were investigated. In order to investigate the hydrogen efficiency, 50 ml of water was added at 850 °C. The detailed reaction conditions can be illustrated in Table 1.

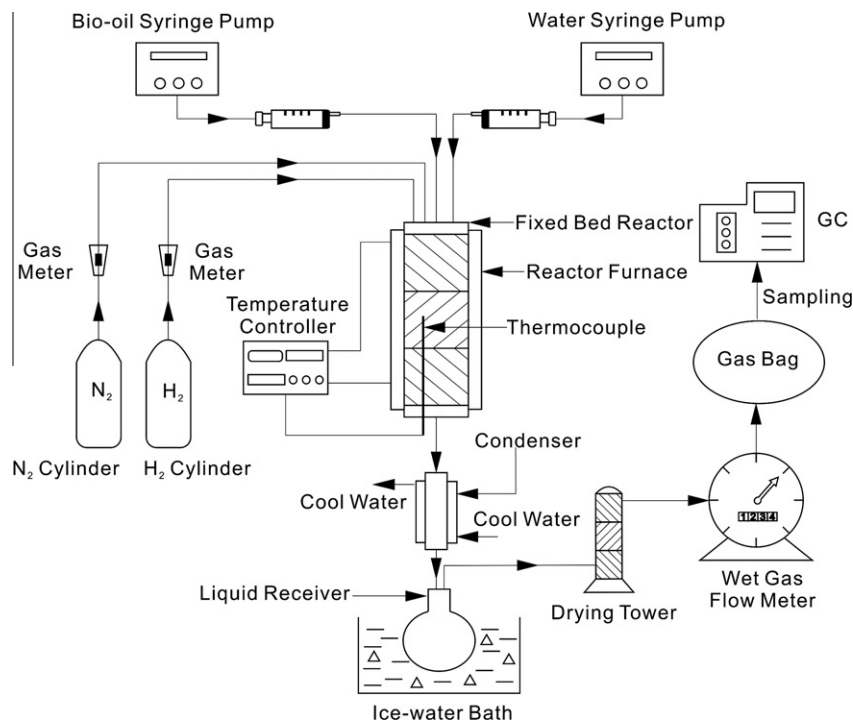


Fig. 1. Schematic diagram of experimental apparatus for catalytic steam reforming of bio-oil.

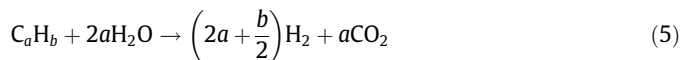
Table 1
Reaction conditions in steam reforming of bio-oil.

Bio-oil	T (°C)	Bio-oil feeding rate (ml/h)	Weight of the chemical compounds (g)	Water feeding rate (ml/h)	Catalyst content (g)	Reaction time (h)
C ₁ ^a	650/750/850	30	11.43	0	10	1
F ₁ ^b	650/750/850	30	7.77	0	10	1
C ₁	850	30	11.43	50	10	1
F ₁	850	30	7.77	50	10	1

^a C₁ – the bio-oil condensed in the condenser without HVF.

^b F₁ – the bio-oil condensed in the condenser with HVF.

The temperature is a great influencing factor on the hydrogen production. In this research, three temperatures (650, 750 and 850 °C) were investigated. The effect of the temperature on the total volume, mole fraction of the gas product, and water content of the liquid condensate is shown in Table 2. From Table 2, it can be seen that total volume of gas product increased with an increase of the temperature, and the bio-oil C₁ has a higher gas volume than that of the bio-oil F₁. Results in Table 2 also show that the hydrogen contents of gas product mole fraction of C₁ bio-oil steam reforming were 60.5, 59.1 and 56.8 vol% at 650, 750 and 850 °C, respectively. The same trend is seen with hydrogen contents of gas product mole fraction of F₁ bio-oil steam reforming, which were 60.3, 59.0 and 55.8 vol% at 650, 750 and 850 °C, respectively. The volume fraction of the H₂ and CO decreased with the increase of temperature. Garcia et al. (2000) reported that the mole fraction of H₂ decreased with the time. This is because the catalyst activity gradually reduced with the time (Xu et al., 2010; Seyedeyn-Azad et al., 2011). Yan et al. (2010a,b) reported that the mole fraction of the H₂ can be from 53% to 62% at all reaction conditions. The volume fraction of CH₄ increased with the increase of temperature. The C₂–C₄ gases were also detected in the gas product. The gas product has the largest yield of C₂–C₄ gases at 850 °C. The existence of CO, CH₄ and C₂–C₄ gases can decrease the hydrogen mole fraction of gas product. The reactions can be illustrated by Eqs. (3)–(5).



Because chemical compounds in the bio-oil are C, H, and O compounds, the molecular formula of C₁ and F₁ are CH_{2.54}O_{0.64} and CH_{3.24}O_{0.78}, respectively. The hydrogen efficiency can be calculated according to Eq. (1). The effect of the temperature on the hydrogen volume and efficiency of steam reforming of bio-oils are shown in Table 3. As can be seen from Table 3, the hydrogen volume and efficiency increased with the increase of the temperature. The C₁ bio-oil produced more hydrogen than that of F₁, but its H₂ efficiency is lower than that of F₁ at the same temperature. Among all the experimental conditions, F₁ bio-oil had the highest H₂ efficiency of 41.07% at 850 °C. The results show that the bio-oil with lower content of chemical compounds has a higher H₂ efficiency, but its hydrogen volume will be decreased. Thus, high temperature is favorable for steam reforming of bio-oil to produce hydrogen.

3.2. Bio-oil steam reforming for hydrogen with addition of water

In order to improve the H₂ efficiency, 50 ml of extra water was added to the reactor at 850 °C. The results show that the total gas product volumes from C₁ and F₁ bio-oils were 19.5 and 13.7 L, respectively. From Table 2, it can be seen that the hydrogen mole fractions from steam reforming of C₁ and F₁ bio-oils were 61.3% and 58.9%, respectively. Based on the volume of the hydrogen product, the H₂ efficiency of steam reforming of the bio-oils can be calculated. The H₂ efficiency of steam reforming of the C₁ and F₁ bio-oils was 44.11% and 45.33%, respectively. The results showed that more hydrogen was produced and the efficiency of steam reforming of the C₁ and F₁ bio-oils was also increased when 50 ml water was added. The mole fraction of CO, CH₄ and C₂–C₄ gases decreased when 50 ml water was added at 850 °C, and the

Table 2

The effect of the temperature on the total volume, mole fraction of the gas product, and water content of the liquid condensate.

	Temperature (°C)	Gas volume (L)	H ₂ mole fraction (mol.%)	CH ₄ mole fraction (mol.%)	CO mole fraction (mol.%)	CO ₂ mole fraction (mol.%)	C ₂ –C ₄ 's ^a mole fraction (mol.%)	Water content of liquid condensate (%)
C ₁	650	10.3	60.5	4.7	13.2	21.6	0	84.39
	750	14.7	59.1	5.0	11.7	21.3	2.9	91.37
	850	17.1	56.8	6.2	10.5	20.8	5.7	92.58
	850 ^b	19.5	61.3	5.5	8.1	25.1	0	–
F ₁	650	9.6	60.3	2.4	7.2	20.4	9.7	87.54
	750	11.6	59.0	3.7	6.4	23.5	7.4	91.45
	850	13.1	55.8	3.7	6.1	21.5	12.9	93.87
	850 ^b	13.7	58.9	4.9	5.2	24.9	5.1	–

^a The C₂–C₄'s were C₂H₂, C₂H₄, C₂H₆, C₃H₄, C₃H₆, C₃H₈, C₄H₆, C₄H₈, C₄H₁₀.^b Fifty milliliter extra water was added to the reactor.**Table 3**The effect of the temperature on the H₂ volume and H₂ efficiency of the bio-oil steam reforming.

	Temperature (°C)		
	650	750	850
H ₂ volume of C ₁	6.23	8.69	9.71
H ₂ efficiency of C ₁ (%)	22.99	32.06	35.83
H ₂ volume of F ₁	5.79	6.84	7.31
H ₂ efficient of F ₁ (%)	32.53	38.43	41.07

CO₂ mole fraction increased. When additional water was added to the reactor, the steam/carbon mole ratio (S/C) was increased. The reactions of Eqs. (3)–(5) were demonstrated, which are favorable for hydrogen production. Wu et al. (2010a,b) and Xu et al. (2010) reported that S/C is a key factor for increasing the hydrogen efficiency in the process of steam reforming of bio-oils to produce hydrogen. The higher S/C is very favorable to improve the heat and mass transfers and leads to reactions defined by Eqs. (3)–(5) but shift to the right side will increase the cost of producing hydrogen.

3.3. Liquid condensate analysis

3.3.1. Water content

Liquid condensate is a component of the steam reforming products. Table 2 showed the content of organic compounds decreased with the increase of temperature because liquid condensate contains water and some carbon organic compounds. The organic compounds in liquid condensate will cause two problems. They lead to a wasting of resources and low hydrogen efficiency. The byproducts formed in the reaction and the unreacted materials are also toxic. They will become a threat to the environment (Wu and Liu, 2010a,b). Wu and Liu (2010a,b) reported that the liquid condensate should be recycled to eliminate these chemical compounds.

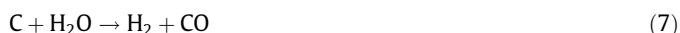
3.3.2. GC–MS analysis

Bio-oil is a complex mixture with a lot of chemical compounds. There were 40 and 38 kinds of compounds detected in the C₁ and F₁ bio-oils, respectively (Chen et al., 2011). GC–MS analysis was carried out to identify the chemical compounds in liquid condensate. Components of liquid condensate from steam reforming of bio-oils and their relative mass contents were detected by GC–MS. The compounds were ordered according to their retention times. The mole fraction of the chemical compounds of liquid condensate was determined by comparing the peak areas and the relative abundance in terms of area percentage. From the results of GC–MS analysis, it can be seen that the liquid condensates from steam reforming of C₁ bio-oil at 650, 750 and 850 °C have large

amounts of the following compounds including phenol (mole fractions were 40.13%, 71.78%, 40.54% respectively), 3-methyl-phenol (mole fractions were 8.02%, 4.44%, 6.01% respectively), 4-methyl-phenol (mole fractions were 15.67%, 14.24%, 19.94%, respectively). The liquid condensates from steam reforming of F₁ bio-oil at 650, 750 and 850 °C have large amounts of phenol (mole fractions were 51.01%, 68.52% and 20.12%, respectively). The main organic compounds of liquid condensate from steam reforming steam reforming of C₁ bio-oil with addition of 50 ml water were: pyridine (mole fraction was 16.66%), phenol (mole fraction was 29.37%), 4-methyl-phenol (mole fraction was 23.47%), 3-ethylphenol (mole fraction was 10.99%). The main organic compound of liquid condensate from steam reforming of F₁ bio-oil with addition of 50 ml water was pyridine (mole fraction was 61.47%). The results show that phenol compounds had the highest mole fraction of all the compounds detected. The mole fraction of pyridine increased with the increase of the temperature. The mole fraction of linear compounds was lower than circularity compounds. This is because the circularity compounds have a steady structure, and they need more energy to react in the steam reforming process.

3.4. Carbon deposition of the catalyst

In process of steam reforming of bio-oil, catalyst deactivation caused by carbon deposition has become a tough question for sustainable hydrogen production (Lan et al., 2010; Wu and Liu, 2010a,b). When carbon deposition occurs, the hydrocarbon can be adsorbed on catalyst surface and decomposed to carbon atoms and carbonaceous atomic groups which can stay on catalyst surface and block metal atoms. The nickel particle is forced to break from the catalyst main body as the carbide grew. Finally, a carbide pillar was formed. Carbon deposition can block the active center of the catalyst and micropores can lead to a decrease of bio-oil conversion. The carbon depositions of steam reforming of bio-oil C₁ were 1.323 g (650 °C), 1.421 g (750 °C), 1.296 g (850 °C), 1.083 g (850 °C with addition of 50 ml water), respectively, and the carbon depositions of steam reforming of bio-oil F₁ were 1.120 g (650 °C), 1.145 g (750 °C), 1.104 g (850 °C), 0.997 g (850 °C with addition of 50 ml water), respectively. From the result, it can be seen that carbon deposition was highest at the middle temperature (750 °C). This is because most carbon organic compounds are condensed to form liquid condensate at the lower temperature, and they can react at higher temperature. When 50 ml water was added at 850 °C, the carbon deposition decreased. In decomposition process of bio-oil, with adequate water in the system, the effect of carbon elimination (the carbon elimination process can be expressed by Eqs. (6)–(8)) can happen. The carbon elimination process can produce more hydrogen, which can enhance the H₂ efficiency of steam reforming of the bio-oil. That is to say, the higher S/C can favor the reaction of carbon elimination.



5. Conclusions

- (1) Mole fractions of H_2 and the CO_2 increased, while the volume fraction of CO , CH_4 and $\text{C}_2\text{--C}_4$ gases decreased with the increase of the temperature from 650 to 850 °C. The highest H_2 efficiency was 45.33% when additional water was added at 850 °C for F_1 bio-oil.
- (2) Bio-oil with lower content of chemical compounds has a higher H_2 efficiency, but its hydrogen volume is decreased.
- (3) Analysis of the liquid condensate showed that most of the organic compounds were circularity compounds.
- (4) Carbon deposition can decrease the bio-oil conversion, and it was more readily formed at 750 °C.

Acknowledgements

Financial support from The National High Technology Research and Development Program of China (863 Program, Grant No. 2008AA05Z404) and financial support from The National Science and Technology Supporting Plan through contract (Grant No. 2011BAD22B07) are greatly acknowledged. In addition, Professor Norman R. Scott from Cornell University, USA is greatly acknowledged for his valuable suggestion and correction of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2011.07.033](https://doi.org/10.1016/j.biortech.2011.07.033).

References

- Bridgwater, A.V., 1999. Principles and practice of biomass fast pyrolysis processes for liquids. *J. Anal. Appl. Pyrol.* 51, 3–22.
- Charles, A., Mullen, A., Akwasi, A.B., 2008. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. *Energy Fuels* 22, 2104–2109.
- Chen, T.J., Deng, C.J., Liu, R.H., 2010. Effect of selective condensation on the characterization of bio-oil from pine sawdust fast pyrolysis using a fluidized bed reactor. *Energy Fuels* 24, 6616–6623.
- Chen, T.J., Wu, C., Liu, R.H., Fei, W.T., Liu, S.Y., 2011. Effect of hot vapor filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor. *Bioresour. Technol.* 102, 6178–6185.
- Chiaromonte, D., Bonini, M., Fratini, E., et al., 2003. Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines – part 2: test in diesel engines. *Biomass Bioenergy* 25, 101–111.
- Fisk, C.A., Morgan, T., Ji, Y., Crocker, M., Crofcheck, C.A., Lewis, S., 2009. Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. *Appl. Catal. A* 358 (2), 150–156.
- Garcia, L., French, R., Czernik, S., Chornet, E., 2000. Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Appl. Catal. A Gen.* 201, 225–239.
- Hyeon, S.H., Hyun, J.P., Young, P., et al., 2010. Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. *Bioresour. Technol.* 101, S91–S96.
- Kim, S.J., Jung, S.H., Kim, J.S., 2010. Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresour. Technol.* 101, 9294–9300.
- Lan, P., Xu, Q.L., Zhou, M., Lan, L.H., Zhang, S.P., Yan, Y.J., 2010. Catalytic steam reforming of fast pyrolysis bio-oil in fixed bed and fluidized bed reactors. *Chem. Eng. Technol.* 33 (12), 2021–2028.
- Lievens, C., Carleer, R., Cornelissen, T., Yperman, J., 2009. Fast pyrolysis of heavy metal contaminated willow: influence of the plant part. *Fuel* 88, 1417–1425.
- Liu, R.H., Deng, C.J., Wang, J., 2010. Fast pyrolysis of corn straw for bio-oil production in a bench-scale fluidized bed reactor. *Energy Source, Part A* 32, 10–19.
- Marquevich, M., Czernik, S., Chornet, E., Montane, D., 1999. Hydrogen from biomass: steam reforming of model compounds of fast pyrolysis oil. *Energy Fuels* 13, 1160–1166.
- Oasmaa, A., Czernik, S., 1999. Fuel oil quality of biomass pyrolysis oils-state of the art for the end users. *Energy Fuels* 13, 914–921.
- Oasmaa, A., Leppamäki, E., Koponen, P., 1997. Physical characterization of biomass-based pyrolysis liquid: application of standard fuel oil analyses. VTT Energy Publication 306.
- Oasmaa, A., Sipilä, K., Solantausta, Y., Kuoppala, E., 2005. Quality improvement of pyrolysis liquid: effect of light volatiles on the stability of pyrolysis liquids. *Energy Fuels* 19, 2556–2561.
- Putun, E., Ates, F., Putun, A., 2008. Catalytic pyrolysis of biomass in inert and steam atmospheres. *Fuel* 87, 815–824.
- Rioche, C., Kulkarni, S., Meunier, F.C., Breen, J.P., Burch, R., 2005. Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Appl. Catal. B Environ.* 61, 130–139.
- Seon, K., Su, J., Joo, K., 2010. Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresour. Technol.* 101, 9294–9300.
- Seyedeyn-Azad, F., Salehi, E., Abedi, J., Harding, T., 2011. Biomass to hydrogen via catalytic steam reforming of bio-oil over Ni-supported alumina catalysts. *Fuel Process. Technol.* 92, 563–569.
- Shen, D.K., Gu, S., Bridgwater, A.V., 2010. The thermal performance of the polysaccharides extracted from hardwood: cellulose and hemicellulose. *Carbohydr. Polym.* 82, 39–45.
- Smith, J., Garcia, M., Das, K.C., 2009. Producing fuel and specialty chemicals from the slow pyrolysis of poultry DAF skimmings. *J. Anal. Appl. Pyrol.* 86, 115–121.
- Takanabe, K., Aika, K., Seshan, K., Lefferts, L., 2004. Sustainable hydrogen from bio-oil-steam reforming of acetic acid as a model oxygenate. *J. Catal.* 227, 101–108.
- Takanabe, K., Aika, K., Seshan, K., Lefferts, L., 2006a. Catalyst deactivation during steam reforming of acetic acid over Pt/ZrO₂. *Chem. Eng. J.* 120, 133–137.
- Takanabe, K., Aika, K., Seshan, K., Lefferts, L., 2006b. Steam reforming of acetic acid as a biomass derived oxygenate: bifunctional pathway for hydrogen formation over Pt/ZrO₂ catalysts. *J. Catal.* 243, 169–263.
- Tsai, W.T., Lee, M.K., Chang, Y.M., 2007. Fast pyrolysis of rice husk: product yields and compositions. *Bioresour. Technol.* 98, 22–28.
- Wang, D., Czernik, S., Chornet, E., 1998. Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. *Energy Fuels* 12, 19–24.
- Wu, C., Liu, R.H., 2010a. Carbon deposition behavior in steam reforming of bio-oil model compound for hydrogen production. *Int. J. Hydrogen Energy* 35, 7386–7398.
- Wu, C., Liu, R.H., 2010b. Hydrogen production from steam reforming of m-Cresol, a model compound derived from bio-oil: green process evaluation based on liquid condensate recycling. *Energy Fuels* 24, 5139–5147.
- Wu, C., Liu, R.H., 2011. Sustainable hydrogen production from steam reforming of bio-oil model compound based on carbon deposition/elimination. *Int. J. Hydrogen Energy* 36, 2860–2868.
- Wu, C., Huang, Q., Sui, M., Yan, Y., Wang, F., 2008a. Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system. *Fuel Process. Technol.* 89 (12), 1306–1316.
- Wu, C., Sui, M., Yan, Y., 2008b. A comparison of steam reforming of two model bio-oil fractions. *Chem. Eng. Technol.* 31 (12), 1748–1753.
- Xu, Q.L., Lan, P., Zhang, B.Z., Ren, Z.Z., Yan, Y.J., 2010. Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a fluidized-bed reactor. *Energy Fuels* 24, 6456–6462.
- Yamazaki, T., Matsuki, K., 2006. Steam reforming reaction of biomass-derived substances over nanoporous Ru/ZrO₂ catalysts (part 1) steam reforming reaction of acetic acid. *J. Jpn. Petrol. Inst.* 49, 246–255.
- Yan, C.F., Cheng, F.F., Hu, R.R., 2010a. Hydrogen production from catalytic steam reforming of bio-oil aqueous fraction over Ni/CeO₂–ZrO₂ catalysts. *Int. J. Hydrogen Energy* 35, 11693–11699.
- Yan, C.F., Hu, E.Y., Cai, C.L., 2010b. Hydrogen production from bio-oil aqueous fraction with in situ carbon dioxide capture. *Int. J. Hydrogen Energy* 35, 2612–2616.